

[Second Edition.]

RESERVE COPY.

## PATENT SPECIFICATION



Application Date : Feb. 14, 1944. No. 2713/44.

582,147

Complete Specification Accepted : Nov. 6, 1946.

## COMPLETE SPECIFICATION

## An Improved Process for the Treatment of Plant Flesh, and the Recovery of Pectic Products therefrom.

We, AFRICAN SISAL & PRODUCE COMPANY LIMITED, a British Company, CONRAD LAWRENCE WALSH, a British Subject, ELSIE LILIAN JAMES, a British Subject, all of Bulstrode, Gerrards Cross, Buckinghamshire, and THOMAS PERCY HOAR, a British Subject, of 5c, Market Hill, Cambridge, Cambridgeshire, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to an improved process for the treatment of plant flesh and the recovery of pectic products therefrom, and has more particular reference to the utilisation of the fleshy material obtained from the sisal plant and like vegetable matter including sansevieria and phormium tenax.

In the commercial extraction of fibres from sisal and like plants, whether the extraction be by wet or dry decortication, or as a result of retting, or of a chemical or mechanical separation of the fibres from the leaf or plant flesh, there remains a considerable bulk of vegetable matter coupled with a small percentage of fibre which is normally a waste product. It is the purpose of our present invention to provide improvements in the treatment and utilisation of this flesh material for the recovery of definite commercial products.

Our analyses of and experiments upon this fleshy material have shown that it contains a variety of materials of commercial value and *inter alia* water soluble materials of a glucosidic and also of a protein-like nature; pectic substances; and ligno-cellulose.

It is known that if the flesh of vegetable matter be extracted with either hot or cold water a large number of water soluble products are extracted from the flesh, which products contain glucosides, tannins and like water soluble vegetable compounds. It is also known that if a subsequent pectic extraction is desired, it is undesirable for the water so used to

[Price 1s.]

have alkaline reagents present as these tend to extract pectic products. Such extractions of pectic products tend to be contaminated with unextracted vegetable matter, which is deleterious to many pectic salts and generally to the appearance of the final product. One of the objects of the present invention is to reduce the raw material to a definite state of purity and freedom from undesirable colouring matter, and to produce extracts of pectic substances of considerable purity and not prejudiced by the presence of undesirable compounds or colouring matter.

It has to be remembered that all vegetable products after severance from the live plant suffer or tend to suffer derogatory change induced by fermentation, enzyme action, degradation under actinic influences and the like and these augment or tend to augment factors inhibitory to extraction present in the fresh cut vegetation.

An object of the present invention is to remove by a controlled pre-treatment of the flesh the said inhibitory factors enabling much larger and more stable yields of products to be obtained, all having an improved appearance, colour and analysis.

It is a further object of the invention to provide processes suitable for the extraction, from the flesh so pre-treated, of the pectic products therein, said extraction by the processes now to be described being more complete, and the products purer and of better physical properties, than have heretofore been possible.

The invention consists in an improved process for the treatment of plant flesh of the type above indicated and for the recovery of pectic products therefrom, characterised that the flesh as stripped from the fibrous backbone of the plant is subjected to a pre-treatment process comprising leaching by water for a period of time dependent upon temperature and upon the amount of the water soluble materials resident in the flesh, washing the leached flesh with water if necessary and adding a bleaching agent e.g. sodium hypochlorite to the leach or wash water,

Price 4s 6d

if necessary treating said flesh with an acid agent having a soluble calcium salt without extraction of pectic products, e.g. hydrochloric acid, rewashing said flesh, and thereafter using said flesh so pre-treated for obtaining alkali metal pectates, ammonium pectate, pectic acid and insoluble metallic pectates and pectin.

The dewatered flesh remaining from the above pretreatment process or processes is in a very suitable condition for the extraction of the pectic products and this embraces the production of alkali-metal pectates, of other metallic pectates, of ammonium pectate and pectin as set out hereafter.

Pectic products or substances as herein described are to be understood to include all those polymeric substances occurring in or latent in the plant flesh that are characterised by giving rise on depolymerisation to galacturonic acid, galactose, arabinose and related compounds. They consist essentially of polygalacturonic acids, with or without galactans and arabans in physical admixture or chemical association, and the simple derivatives thereof, such as the salts of polygalacturonic acid, and the methyl esters of polygalacturonic acid including the partially methylated esters of that acid that are known as pectins or pectinic acids.

A preferred manner of operating the invention is set out below with a series of practical examples, but wherein it may be necessary to make appropriate small deviations from the figures given to allow for (a) age of plant, (b) soil in which it has grown, (c) season of cutting, (d) type of decortication, (e) period of delay between cutting and process treatment. Examples 1 to 6 refer to the pretreatment processes, Examples 7 to 10 to the extraction processes we have found to be suitable for the pre-treated flesh.

#### EXAMPLE 1.

The flesh is leached with 15 to 30 times its weight of water, preferably soft water, for 24 hours at 10° C. to 20° C., preferably with agitation, and is then separated from the liquor by draining, and washed if desired with more water.

#### EXAMPLE 2.

The flesh is leached with 15 to 30 times its weight of water, preferably soft water, for  $\frac{1}{4}$  to  $\frac{1}{2}$  hour at 80° C. to 100° C., preferably with agitation, and is then separated from the liquor by draining, and washed if desired by more water. It is understood that lower temperatures such as 30° C. to 75° C. may be used when correspondingly longer periods of time for leaching should be allowed.

#### EXAMPLE 3.

To the leaching water as in Examples 1 or 2 is added a quantity of a bleaching agent such as sodium hypochlorite, preferably before the addition of the flesh. We have found that a suitable amount is  $4\frac{2}{5}$  pints of commercial sodium hypochlorite solution of 15% strength to every 60 to 70 gallons of leaching water, but it will be understood that the amount to be used will depend on the colour and condition of the flesh being processed and may have to be determined on each batch by trial.

#### EXAMPLE 4.

To the washing water as in Examples 1 or 2 is added a bleaching agent such as sodium hypochlorite, as described in Example 3. A further wash with water may be given if desired.

#### EXAMPLE 5.

To the leaching water as in Example 1 is added 2% to 5% by volume of commercial concentrated hydrochloric acid and the leaching is allowed to proceed for  $\frac{1}{4}$  to 5 hours. This treatment results in a change in the pectic substances within the flesh, but does not produce their extraction; and on washing out the excess acid and proceeding to any of the pectic extractions as set out in Examples 7 to 10 we find that these are made easier in every case, in that they proceed to completion at lower temperatures and in some cases in less time. Furthermore in the extraction of pectate, alkalies not containing calcium-precipitating anions can be used, for instance sodium hydroxide; and in the extraction of pectin, more dilute reagents can be used, doubtless because the acid soaking removes a good deal of the calcium from the flesh by breaking down calcium pectate linkages and dissolving any free calcium carbonate. Suitable amounts and conditions are:—

	Parts by weight.
Flesh — — — — —	1
0.5 N Hydrochloric acid — —	15

used cold for three hours. The resulting flesh after being washed with cold water to remove excess hydrochloric acid gives immediate extraction of some pectate in the cold and a good yield at 80° C. when processed according to Example 7. The dilute hydrochloric acid may be removed and used over again.

#### EXAMPLE 6.

To the washing water as in Examples 1 or 2 is added hydrochloric acid as described in Example 5 and the dilute

acid is maintained in contact with the flesh for  $\frac{1}{2}$  to 5 hours at room temperature, after which it is washed out with more water. This acid wash may also be applied to the flesh first treated either according to Example 3 or 4, if an intermediate wash with water is given to remove excess sodium hypochlorite before the addition of acid.

#### EXAMPLE 7.

The flesh pre-treated according to any of Examples 1 to 6 is mixed with a solution of an alkali-metal or ammonium salt having an alkaline reaction, of which the anion gives an insoluble salt with calcium ions. Thus sodium carbonate or trisodium phosphate or sodium metasilicate are suitable extracting agents. The effect of the extracting agent is twofold; it hydrolyses any methoxy groups in the protopectin of the plant material, and it decomposes any calcium pectate linkages in the protopectin with the formation of an insoluble calcium salt; the alkali-metal salt of pectic acid is thus produced and this dissolves colloiddally in the aqueous extracting solution. Convenient amounts of the materials are:—

	Parts by weight.
Flesh — — — — —	1
Water — — — — —	30
Sodium Carbonate (anhydrous)—	0.2

the extraction being carried on for 15 to 30 minutes at 60° C. to 100° C. with stirring. It will be understood that these amounts, times and temperatures are given by way of example only and may be widely varied according to the particular sample of raw material, the conditions obtaining at the factory, for example, the amount of time, fuel and sodium carbonate available, and the nature of the product desired. Indeed, the extraction using the above formula may be made in the cold, at say 20° C. if the time allowable is of the order of 24 hours, and if the highest percentage yield is not a prime consideration.

It should be understood that the amount of "flesh" specified in this Example and all other Examples herein refers to the original weight of air-dry flesh taken before pre-treatment.

When trisodium phosphate is used for the extraction this may particularly well be made at comparatively low temperatures, a convenient formula being:—

	Parts by weight.
Flesh — — — — —	1
Water — — — — —	30
Trisodium Phosphate — — — — —	0.25

used at a temperature of 30° C. with stirring, for  $\frac{1}{2}$  to 2 hours.

The alkali-metal pectate sol resulting from either of these extractions or equivalent processes using other suitable alkali-metal salt solutions, is filtered off, and from it is precipitated either:—

(q) Alkali-metal pectate, which may be produced either by the addition of alcohol, acetone or like water-miscible organic solvent, or by the addition of a concentrated solution of sodium chloride (say 30/35% by weight), sodium sulphate or other electrolyte that does not react with the alkali-metal pectate. The gelatinous precipitate of alkali-metal pectate is collected, dried and ground, and is then a marketable product taking the form of a white or nearly white powder, readily dispersible in water to form viscous solutions or gels; the whiteness of the product may be improved by adding a small proportion of sodium hypochlorite solution before or during the precipitation.

(b) Pectic acid which may be produced by the addition of any acid (hydrochloric acid being suitable) having a dissociation constant greater than about  $10^{-4}$ , to the alkali-metal pectate sol; a flocculent precipitate is produced which is collected by settlement or filtration, and which is dried and powdered as under (a). It is a nearly white powder soluble in alkaline solutions, sparingly soluble in water. When the extraction has been made with sodium metasilicate the pectic acid floc may contain also silicic acid.

(c) Metallic pectates, produced by the addition of a dilute solution of a water-soluble metallic salt to the alkali-metal pectate sol, whose pH has previously been brought to a value of about between 6 and 8 by the cautious addition of an acid such as hydrochloric, nitric or acetic acids, and from which adjusted solution excess carbon dioxide (in the case of an extraction made with sodium carbonate) has preferably been boiled off or blown off with a current of air, and which has preferably been diluted if necessary so that it contains not more than  $\frac{1}{2}$ % of pectate; for example, zinc chloride, nickel chloride, silver nitrate or calcium chloride solutions may be added to give zinc pectate, nickel pectate, silver pectate and calcium pectate respectively as flocculent precipitates which may be removed, dried and powdered as before. These pectates are insoluble in water.

When it is desired to prepare ammonium pectate, this may be produced as a sol by the dissolution of pectic acid in ammonia or directly from the flesh by extraction with a solution of ammonium

phosphate, under the same conditions as those stated above for trisodium phosphate, except that the temperature should be about 20° C. higher.

5

## EXAMPLE 8.

If the extraction of the flesh pre-treated according to any of Examples 1 to 6 is carried out by means of a solution of an alkali-metal salt having an anion that forms water-soluble complexes with calcium, then if the solution has a pH below 7, pectin is extracted, whereas if the solution is substantially alkaline, alkali-metal pectate is the product. Such alkali-metal salts are the hexametaphosphates, pyrophosphates and the like, and a suitable formula for making the pectin extraction is:—

	Parts by weight.
Flesh — — — — —	1
Acid Sodium Hexametaphosphate — — — — —	0.1
Water — — — — —	30

25 used at boiling point for 5 to 30 minutes. The same formula, but with the liquor adjusted to pH 9–10 with sodium hydroxide or other alkali, may be used to give an extract of sodium pectate. From the sols produced, alkali-metal pectate is obtained in the dry condition by means of processes similar to those already set out or referred to, in Example 7, while pectin is obtained by salting out or by 35 other known means.

## EXAMPLE 9.

When the flesh has been pre-treated according to Examples 5 or 6, the extraction of pectic substances may be achieved by the use of alkaline solutions not containing anions forming insoluble calcium salts or soluble calcium complexes. Thus ammonia or the alkali-metal hydroxides may be used. The conditions as to amounts, times and temperatures may be widely varied, but are in general similar to those given in Examples 7 and 8 for alkali-metal hydroxides, but for ammonia extractions 50 the temperature should not exceed 40° C. In particular, it may be mentioned that partial extraction by ammonia solution can be achieved under the following conditions:

	Parts by weight.
Flesh — — — — —	1
Water — — — — —	30
Ammonia (S. Gr. 0.880) — — — — —	0.5

60 used at room temperature for  $\frac{1}{2}$  hour.

## EXAMPLE 10.

The flesh pre-treated according to any of Examples 1 to 6 is in a very favourable condition for the extraction of pectin. In particular, a suitable formula is:—

65

	Parts by weight.
Flesh — — — — —	1
Ammonium Oxalate — — — — —	0.3
Water — — — — —	40

70

the liquor being adjusted to pH 5 or thereabouts by the addition of oxalic acid, and used at 60° C. for  $\frac{1}{2}$ -hour. The pectin sol so produced is filtered from the flesh, preferably on a filter primed with kieselguhr, and from it pectin is recovered by salting out, by the use of alcohol or the like, by precipitation with aluminium hydroxide, or by other known means. It will be understood that some yield of pectin may be obtained by treatment of the pre-treated flesh with any warm or hot aqueous electrolyte having a pH of about 5 or less, but that the conditions stated above have been found especially suitable for the particular pre-treated flesh herein described. 75

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:— 80

1. An improved process for the treatment of plant flesh of the type above indicated and for the recovery of pectic products therefrom characterised that the flesh as stripped from the fibrous backbone of the plant is subjected to a pre-treatment process comprising leaching by water for a period of time dependent upon temperature and upon the amount of the water soluble materials resident in the flesh, washing the leached flesh with water if necessary and adding a bleaching agent, e.g. sodium hypochlorite to the leach or wash water, if necessary treating said flesh with an acid reagent having a soluble calcium salt without extraction of pectic products, e.g. hydrochloric acid, rewashing said flesh, and thereafter using said flesh so pretreated for obtaining alkali metal pectates, ammonium pectate, pectic acid and insoluble metallic pectates and pectin. 85 90 95 100 105 110

2. In a process for the treatment of plant flesh as claimed in Claim 1, in which the acid having a soluble calcium salt, such as hydrochloric acid, is added to the said leaching water, the leaching water being in this case at room temperature. 115 120

3. In a process for the treatment of plant flesh as claimed in Claim 1, in

which the acid having a soluble calcium salt, such as hydrochloric acid, is added to the said washing water, the washing water being used at room temperature.

5 4. In a process for the treatment of plant flesh as claimed in Claims 2 and 3, washing the flesh with water and then with a cold dilute solution of an acid having a soluble calcium salt.

10 5. A process for the treatment of plant flesh wherein the flesh, pre-treated according to any of Claims 1 to 4 is treated with an aqueous solution of an alkali-metal or an ammonium salt having an alkaline reaction and having an anion that gives an insoluble calcium salt, with the production of an alkali-metal or ammonium salt of pectic acid that is colloiddally soluble in the aqueous extracting solution, and collecting said colloidal sol from the treated mass by filtration.

20 6. A process for the treatment of plant flesh wherein the flesh, pre-treated according to any of Claims 1 to 4 is treated with an aqueous solution of an alkali-metal salt having an alkaline reaction and having an anion that gives a soluble calcium complex, with the production of an alkali-metal salt of pectic acid that is colloiddally soluble in the aqueous extracting solution, and collecting said colloidal sol from the treated mass by filtration.

30 7. A process for the treatment of plant flesh wherein the flesh, pre-treated according to any of Claims 2, 3 or 4 is treated with an aqueous solution of an alkali-metal or an ammonium compound, having an alkaline reaction, with the production of an alkali-metal or ammonium salt of pectic acid that is colloiddally soluble in the aqueous extracting solution, and collecting said colloidal sol from the treated mass by filtration.

40 8. In a process for the treatment of plant flesh as claimed in Claims 5, 6 or 7, the additional step of converting said sol to a gel by the addition of an electrolyte, e.g., sodium chloride, that does not react with an alkali-metal pectate, or by the addition of a water miscible organic solvent, collecting the precipitated gel, drying and powdering same, and producing a white or off-white powder therefrom.

55 9. In a process as claimed in Claims 5, 6 or 7, the additional step of producing pectic acid gel by treating the alkali-metal pectate sol with the addition of an

acid having a dissociation constant greater than about  $10^{-4}$ , filtering the mass and drying and powdering the resultant precipitate. 60

10. In a process as claimed in Claims 5, 6 or 7, the additional step of producing metallic pectates from the alkali-metal pectate sol by treating said sol with a suitable acid and as described under Example 7 (c) to bring it to a pH of about between 6 and 8, driving off any excess  $\text{CO}_2$ , diluting the acidified mixture to a 0.25% content of pectate salt, adding a dilute aqueous solution of a soluble metallic salt to obtain a precipitated metallic pectate of the variety set forth and collecting, drying and grinding the precipitate. 65 70 75

11. A process for the treatment of plant flesh wherein the flesh, pre-treated according to any of Claims 1 to 4, is treated with an aqueous solution of an alkali-metal salt not having an alkaline reaction, but having an anion that forms soluble calcium complexes, with the production of a colloidal sol of pectin or of methylated esters of polygalacturonic acid, and of collecting said sol from the treated mass by filtration. 80 85

12. A process for the treatment of plant flesh wherein the flesh, pre-treated according to any of Claims 1 to 4, is treated with an aqueous electrolyte which is adjusted to a pH of about 5 or less with the production of a sol of pectin or of methylated esters of polygalacturonic acid, and of collecting said sol from the treated mass by filtration. 90 95

13. A process for the treatment of plant flesh wherein the flesh pre-treated according to Claim 2, 3 or 4, is subjected to an extraction process for the recovery of pectic substances comprising, the step of subjecting said flesh to an alkaline solution not containing anions forming insoluble calcium salts, or soluble calcium complexes, such as ammonia used at a temperature not exceeding  $40^\circ \text{C}$ . or alkali-metal hydroxides used at temperatures up to  $100^\circ \text{C}$ . 100 105

14. Pectic substances as herein defined when produced by any of the processes herein described and claimed. 110

Dated this 14th day of February, 1944.

HERON ROGERS & CO.,

Agents for the Applicants,  
Bridge House, 181, Queen Victoria Street,  
London, E.C.4.